Study of several approaches for predicting electrical conductivity of sodium-dodecyl-sulfate solution in the presence of Na₂CO₃ and KPS

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ABSTRACT

In this paper, semi-empirical relationships for calculating the electrical conductivities of *sodium dodecyl sulfate* (SDS) solutions in the presence of different concentrations of *sodium carbonate* and *potassium persulfate* (KPS), which are used in emulsion polymerization, are given. The results of these methods for predicting the electrical conductivities are given and compared with each other and with experimental data. Finally, a new method for conductivity prediction is presented. The new method, based on this study, predicts the conductivity of electrolyte solutions more accurately, especially in a moderate or relatively high concentration of electrolytes. Hence, to show the superiority of this method compared to previous methods, the conductivities of different concentrations of combinations of these electrolytes were evaluated and compared with the previous methods. Similarly, the effects of the concentration of electrolytes on electrical conductance of SDS solutions above and below the critical micelle concentration (CMC) are studied.

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1. Introduction

Electrical conductivity is one of the main transport properties of aqueous electrolyte systems. The electrical conductivity of solutions and its dependence on temperature, concentration, and chemical nature of the solvents is an interesting issue in both theoretical and technological fields due to various applications. For instance, in engineering applications, information of the electrical conductivity is significant for the design and optimization of diverse processes and devices, particularly those relating to electrochemical systems, such as electrolysis equipments and high-performance batteries [1,2]. In addition, the conductance of electrolyte solutions is one of the most considerable factors in lithium ion batteries, where the electrolyte comprises lithium salts (e.g. LiPF₆) in organic solvent solutions [3]. Moreover, the calculation of the electrical conductivity of concentrated aqueous electrolyte solutions is helpful for many industrial processes such as plating, material transport, solid deposition, and corrosion protection [4]. In the area of corrosion protection, electrical conductivity provides useful knowledge for estimating the corrosivity of aqueous media and for the design of cathodic protection systems. Electrical conductivity can also be used to gain insight into the properties of electrolyte solutions and to determine characteristic physical quantities, such as dissociation constants [1,2].

The practicable significance of the electrical conductivity and the theory of electrolyte solutions have attracted increasing interest of researchers, due to the large quantity of experimental results published freshly [2,3,5,6]. However, little attention has been paid to the development of a model and some reasonable coefficients to calculate the electrical conductivity of the electrolyte solutions that are widely used in emulsion polymerization systems, such as solutions with initiators or buffers, especially at 60 °C (reaction temperature). The model should be accurate not only at low concentrations but also in high concentration systems. In particular, to the best of our knowledge, no effort has been made to declare a semi-empirical relationship or a model with reasonable coefficients for predicting the electrical conductivity of Na₂CO₃ and KPS solutions that are crucial materials in emulsion polymerization, when Na₂CO₃ and KPS solutions are used as buffer and initiator, respectively. It is worth noting that the absence of Na₂CO₃ in the emulsion polymerization of butadiene, with SDS as a surfactant, causes the reaction to go very slowly. Also, little attention has been paid to the prediction of the effect of concentration on the electrical conductivity of the SDS solution above and below the critical micelle concentration (CMC), especially with these electrolytes.

The objective of this study is to declare a semi-empirical relationship and some reasonable coefficients for some models shown in the literature to predict electrical conductivity of important solutions used in emulsion polymerization at 25 °C and 60 °C. The main goal of this article is to propose a new method for predicting the electrical conductivity of solutions, which is accurate not only in low concentration solutions but also in moderate or relatively high concentration aqueous electrolyte solutions at emulsion polymerization reaction temperature, and in addition, to predict the effect of concentration on the electrical conductance of SDS solutions above and below the CMC. Finally, obtained results were compared with the experimental data.

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2. Experiments

The salts Na$_2$CO$_3$ (Applichem, 99.5 +%) and KPS (Merck, 99 +%) were used. Distilled water was used to prepare the solutions. SDS (Merck, 99 +%) was used as received without further purification.

In this study, a radiometer CDM210 conductometer with a radiometer conductivity cell was used. The conductivity cell was calibrated by measuring the conductivity of *KCl* solutions at various concentrations. Experiments took place by adding diverse amounts of surfactant solution to a fixed volume of electrolyte solution and measuring the conductivity.

3. Results and discussion

3.1. Estimation of electrical conductivity of SDS solutions with different concentrations of KPS and Na$_2$CO$_3$ electrolytes

To estimate the solution conductivity derived from the concentration of surfactant ions, counterions, and micelles, semi-empirical models are submitted. Fig. 1 displays the experimental data for conductometric SDS titration of distilled deionized water at 25 °C and 60 °C. In this figure, alteration of the slope of the titration curve is attributed to the saturation point where micelles start to form (i.e., the CMC) [7]. It is presumed that the aqueous surfactant solution is conformed to Kohlrausch's law. Therefore, the computed electrolyte conductivity

σ_{calc} (mS/cm) can be expressed as a weighted sum of the equivalent conductivity λ_i (mS cm^2/mmol) of each ionic species [1,2,8].

$$\sigma_{calc} = \sum z_i c_i \lambda_i \tag{1}$$

The quantities z_i and c_i (mmol/cm^3 or mol/L) are the species valence and aqueous molar concentration, respectively. For pure aqueous SDS solution, the electrolyte conductivity σ_{calc} can be determined as the sum of the corresponding molar equivalent conductivities of Na$^+$ (λ_{Na^+}) and DS$^-$ (λ_{DS^-}) ions according to [9,10]:

$$\sigma_{calc} = \lambda_{Na^+}\left[Na^+\right] + \lambda_{DS^-}[DS^-]. \tag{2}$$

In what follows, the changes of conductivity with SDS concentration, which is depicted in Fig. 1 at 25 °C and 60 °C, are described. For a given SDS concentration below the CMC (line 1), when there is no micelle, the surfactants act as strong electrolytes at very low concentrations. Consequently, it is reasonable to presume the perfect dissociation of the SDS, that is, $[Na^+] = [DS^-] = [S_T]$, where $[S_T]$ represents the total concentration of surfactant and the electrical conductance of the solution is then given by [11,12]:

$$\sigma_{calc} = (\lambda_{Na^+} + \lambda_{DS^-})[S_T] \tag{3}$$

where $(\lambda_{Na^+} + \lambda_{DS^-})$ is the slope of line 1 in Fig. 1. In the cases that concentrations are above the CMC (line 2), the solution conductivity is evaluated from the following equations [12]:

$$\sigma_{calc} = (\lambda_{Na^+} + \lambda_{DS^-})CMC + \frac{([S_T]-CMC)}{a}\lambda_{Na^+} \tag{4}$$

$$= \left(\frac{(a-1)}{a}\lambda_{Na^+} + \lambda_{DS^-}\right)\left[S_{aq}\right] + \frac{\lambda_{Na^+}}{a}[S_T] \tag{5a}$$

$$\left[S_{aq}\right] = \begin{cases} [S_T] & [S_T]<CMC \\ CMC & [S_T]>CMC \end{cases} \tag{5b}$$

where $\frac{\lambda_{Na^+}}{a}$ is the slope of line 2 in Fig. 1. It should be noted that the effective factors, such as the addition of electrolytes, temperature, addition of organic modifiers, ionic strength of the aqueous solution, and presence of additives can change the CMC value from that of determined in pure water. Therefore, a comprehensive investigation has been done, by the authors of this paper, on the micellization behavior of SDS with different electrolytes, such as Na$_2$CO$_3$ and KPS electrolytes in different temperatures [13].

In concentrations above the CMC, the superfluity surfactant molecules aggregate in the aqueous phase, and micelles are shaped by DS$^-$
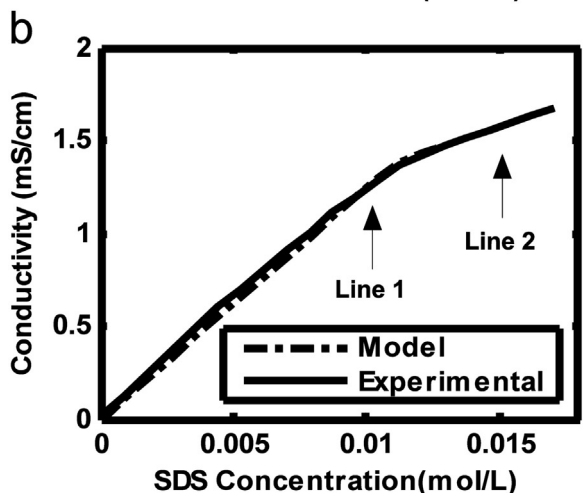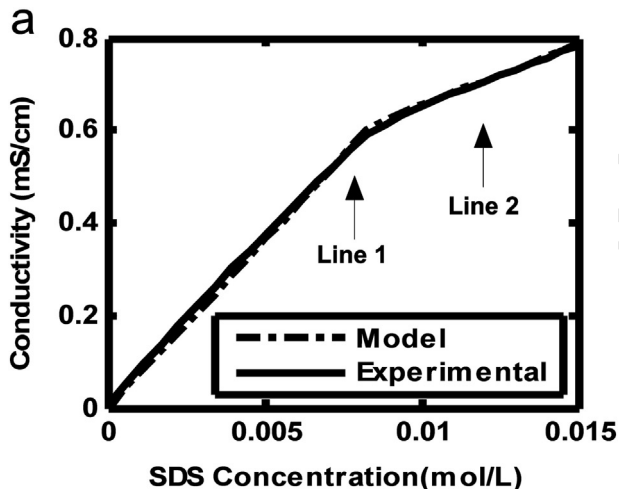

Fig. 1. Model prediction and experimental conductivity data for SDS titration of distilled deionized water at a) 25 °C and b) 60 °C.
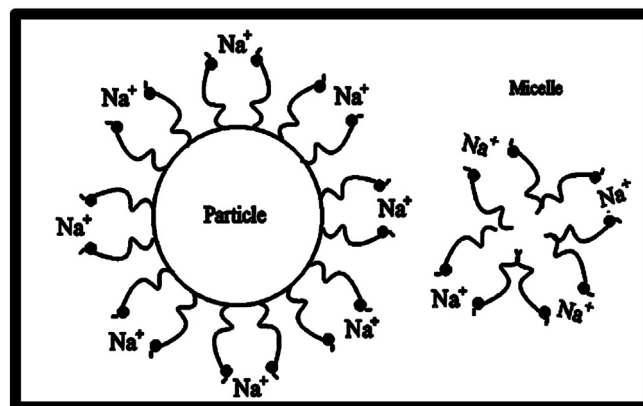

Fig. 2. Surfactant adsorption on polymer particles and surfactant aggregation for micelle formation.